APPLICATION

FOR

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TITLE: **UNIT FOR SEPARATING GAS**

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DESCRIPTION

UNIT FOR SEPARATING GAS

5   TECHNICAL FIELD

[0001]

The present invention relates to a unit for separating gas, which separates each of a plurality of specific gases from a treatment gas containing the specific gases.

10

BACKGROUND ART

[0002]

Conventionally, a variety of different gases are used in semiconductor production processes, depending on the

15   nature of the individual process. For example, PFC (perfluoro compound) gas, which includes a variety of fluorine-containing compounds ·such as CF_4, NF_3, C_3F_8, SF_6 and CHF_3, is used as a reactive gas in dry etching processes and thin film formation processes, and an exhaust gas containing

20   this PFC gases is produced.

[0003]

Exhaust gases such as PFC gas cannot be simply discharged from the system, and must be treated using a variety of treatment methods. Examples of these treatment

25   methods include (i) decomposition treatments in which the PFC gas is decomposed by combustion, catalytic heating, or plasma decomposition or the like, (ii) membrane separation in which the materials are separated by a membrane, (iii) cryogenic separation in which separation is achieved by

30   utilizing differences in the boiling points of the gases, and (iv) adsorption treatments.

[0004]

However, there are drawbacks associated with decomposition treatments (i) in that achieving complete decomposition is difficult, and the fact that because the gas is decomposed and discharged, it cannot be recovered and reused. Furthermore, although membrane separation (ii) enables the removal of nitrogen from an exhaust gas, the separation of gases of similar molecular size such as CF_4 and NF_3 is problematic. Moreover, the aforementioned method (iii) requires an extremely large apparatus, and is very expensive in terms of both running costs and the cost of the facilities. Furthermore, the difference in boiling point between NF_3 and CF_4 is only 1°C, meaning separation of these two gases is very difficult. The method (iv) requires regular replacement of the adsorbent, which leads to costs associated with the disposal of the used adsorbent.

[0005]

Accordingly, Japanese Patent Laid-Open Publication No. 2002-273144 proposes a device for separating PFC gases that uses a chromatographic separation device packed with an activated carbon filler. The device disclosed in Japanese Patent Laid-Open Publication No. 2002-27314 is able to effectively separate CF_4 and NF_3.

[0006]

However, it was found that the device disclosed in Japanese Patent Laid-Open Publication No. 2002-27314 was unable to satisfactorily separate a mixed gas of CF_4 and C_2F_6, for example. As described above, PFC gas contains a variety of different gases, and a unit that is capable of effectively treating and separating this type of multi-component PFC gas has been keenly sought.

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DISCLOSURE OF INVENTION

[0007]

The present invention provides a unit for separating gas that is capable of effectively separating each of the components from a PFC gas containing a plurality of components.

[0008]

The present invention provides a unit for separating gas, which separates each of a plurality of specific gases from a treatment gas containing the specific gases, wherein the unit contains a plurality of columns packed with different fillers, and by connecting these columns in series, and passing the treatment gas sequentially through the fillers of the plurality of columns, each of the specific gases is separated chromatographically from the treatment gas.

[0009]

Furthermore, the present invention also provides a unit for separating gas, which separates each of a plurality of specific gases from a treatment gas containing the specific gases, wherein the unit contains a column packed with a plurality of different fillers, and by passing the treatment gas through the plurality of fillers inside the column, each of the specific gases is separated chromatographically from the treatment gas.

[0010]

By conducting chromatographic separation using a plurality of fillers in this manner, the plurality of specific gases can be separated effectively.

[0011]

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Furthermore, the aforementioned specific gases are preferably PFC gases discharged from semiconductor production processes, and the aforementioned treatment gas is preferably a gas that also contains nitrogen gas.

[0012]

Furthermore, the specific gases preferably include NF_3, CF_4, and C_2F_6, and the aforementioned fillers preferably include zeolite and activated carbon.

[0013]

Furthermore, the zeolite is preferably the molecular sieve 13X or an equivalent product.

[0014]

As described above, the present invention enables a plurality of specific gases to be separated effectively, by conducting chromatographic separation using a plurality of fillers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 is a diagram showing the structure of an embodiment of the present invention.

Fig. 2 is a diagram showing the structure of a chromatographic separation device that uses a plurality of columns.

Fig. 3 is a graph showing the state of gas flow at the outlet of the first column.

Fig. 4 is a graph showing the state of gas flow at the outlet of the second column.

Fig. 5 is a diagram showing the structure of a chromatographic separation device that uses a plurality of columns.

Fig. 6 is a graph showing the state of gas flow at the outlet of the column shown in Fig. 5.

Fig. 7 is a diagram showing the structure of a test unit.

Fig. 8 is a diagram showing the structure of another test unit.

BEST MODE FOR CARRYING OUT THE INVENTION

[0016]

As follows is a description of a preferred embodiment of the present invention, based on the drawings.

[0017]

A PFC gas is supplied to a production process 10 such as an etching or thin film formation process conducted at a semiconductor production plant. As a result, an exhaust gas containing the PFC gas is produced. An inlet for a suction pump 12 is connected to the path of the exhaust gas, and the exhaust gas containing the PFC gas is extracted from the production process 10 by this suction pump 12. Gases such as CF_4, NF_3, C_2F_4, and SF_6 can be used as the PFC gas, and in this embodiment, the PFC gas contains CF_4, C_2F_6, and NF_3. Because the PFC gas decomposes and generates hydrofluoric acid during the production process 10, the exhaust gas also contains hydrofluoric acid. As a result, if the exhaust gas is introduced directly into the suction pump 12, then there is a danger that the suction pump 12 may be damaged. Furthermore, the exhaust gas also contains metals generated during etching and the like, meaning if the exhaust gas is introduced directly into the suction pump 12, there is a danger that deposits may accumulate inside the suction pump 12. Accordingly, nitrogen (N_2) gas is supplied as a diluent

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gas at a point prior to the exhaust gas reaching the suction pump 12, thereby diluting the exhaust gas.

[0018]

5   The outlet of the suction pump 12 is connected to a scrubber 14, and the nitrogen-diluted exhaust gas is supplied to the scrubber 14. This scrubber 14 uses a water shower to dissolve and remove hydrofluoric acid (HF) and any other water-soluble acidic materials contained within the exhaust gas.

10   [0019]

The exhaust gas from the scrubber 14 is then supplied to a dewatering device 16, where moisture is removed from the gas. The exhaust gas from the scrubber contains a large quantity of moisture, and it is preferable to remove this

15   moisture prior to the subsequent steps. Although any form of dewatering device can be employed as the dewatering device 16, devices that remove the moisture by lowering the temperature of the exhaust gas are preferred.

[0020]

20   The exhaust gas containing the PFC gas and nitrogen is then supplied to a concentration device 18. This concentration device 18 is used for removing the nitrogen, and is preferably a membrane separation device that employs a gas permeable membrane. This device separates the

25   nitrogen from the exhaust gas, thereby concentrating the PFC gas (the CF_4, NF_3, and C_2F_6 in this embodiment).

[0021]

Having been concentrated in this manner, the PFC gas is supplied to a chromatographic separation device 20. The

30   chromatographic separation device 20 includes a column packed with a desired filler, and the gas is passed through

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this column. Because each of the gas components exhibits a different affinity (adsorption and desorption coefficient) for the filler, the retention times for each component vary, thus enabling the gas to be separated into its components.

5 In other words, the CF_4, NF_3, and C_2F_6 are separated. Because nitrogen gas is used as a carrier gas in the chromatographic separation, each gas is generated as a mixed gas with nitrogen.

[0022]

10 At this point, the mixed gas of CF_4 + nitrogen is supplied to a concentration device 22, C_2F_6 + nitrogen is supplied to a concentration device 24, and NF_3 + nitrogen is supplied to a concentration device 26. These concentration devices 22, 24 and 26 are similar to the concentration

15 device 18 described above, and can employ membrane separation devices. Within these membrane separation devices, by employing a structure wherein the concentrated gas is either circulated a number of times, or treated in a plurality of stages, almost 100% of the nitrogen can be

20 separated, meaning pure CF_4 gas, NF_3 gas, and C_2F_6 gas can be obtained at concentrations of 100%.

[0023]

The CF_4 gas, C_2F_6 gas, and NF_3 gas can be recovered and reused within the production process 10.

25 [0024]

As described below, the chromatographic separation device 20 usually also yields a fraction that contains both CF_4 and NF_3, but the CF_4 and NF_3 can be separated by subjecting this mixed fraction to further separation, and

30 consequently this CF_4 + NF_3 fraction has been omitted from the diagram.

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[0025]

In this manner, by using the chromatographic separation device 20, the present embodiment enables CF_4, C_2F_6, and NF_3 gases to be separated effectively. Moreover, the separated

5   CF_4, C_2F_6, and NF_3 gases can be recovered and reused.

[0026]

Fig. 2 shows an example of the structure of the chromatographic separation device 20. In this example, the chromatographic separation device 20 includes two columns,

10   namely a first column 50-1 and a second column 50-2, connected together in series. The first column 50-1 is packed with a zeolite (molecular sieve 13X) 30 with a predetermined pore size, and the second column 50-2 is packed with palm shell activated carbon 32. The first

15   column 50-1 is supplied continuously with nitrogen gas (N_2), and is also supplied intermittently with the treatment gas containing CF_4, NF_3 and C_2F_6 via a valve 34. The outlet of the first column 50-1 is connected to the inlet of the second column 50-2 via a valve 36, and is also able to

20   discharge C_2F_6 gas via a valve 38. In addition, the outlet of the second column 50-2 is able to discharge CF_4 + N_2 gas via a valve 40, CF_4 + NF_3 + N_2 gas via a valve 42, NF_3 + N_2 gas via a valve 44, and nitrogen (N_2) gas via a valve 46.

[0027]

25   In this type of chromatographic separation device 20, first the valves 34, 38, 40, 42 and 44 are closed, the valves 36 and 46 are opened, and the first and second columns 50-1 and 50-2 are flushed with N_2 carrier gas. From this state, the valve 34 is opened, and a predetermined

30   quantity of the treatment gas is supplied in a pulse-like manner. This treatment gas should preferably be supplied to

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the first column 50-1 with minimal dilution by the N_2 gas.
Appropriate switching of the valves may also be used to
temporarily halt the supply of N_2 while the treatment gas is
supplied.

5 [0028]

Following the supply of the predetermined quantity of
the treatment gas, the valve 34 is closed, and the supply of
the N_2 gas can be recommenced. The CF_4, NF_3 and C_2F_6 within
the treatment gas is separated by the molecular sieve 13X

10 inside the first column 50-1. In other words, the C_2F_6 is
slower to desorb from the molecular sieve 13X than the CF_4
and NF_3. Consequently, as shown in Fig. 3, the CF_4 + NF_3
fraction from the treatment gas appears first at the outlet
of the first column 50-1, with the C_2F_6 fraction appearing

15 considerably later.

[0029]

Accordingly, when the C_2F_6 is discharged, the valve 36
is closed and the valve 38 is opened, thus enabling
separation and extraction of the C_2F_6 gas. Once extraction

20 of the C_2F_6 has finished, the valve 38 is closed and the
valve 36 is opened.

[0030]

As a result, the second column 50-2 is supplied with a
treatment gas that contains CF_4 and NF_3, but contains no C_2F_6.

25 In the second column 50-2, the CF_4 and NF_3 are separated by
the activated carbon 32. In other words, the NF_3 is slower
to desorb from the activated carbon than the CF_4.
Consequently, as shown in Fig. 4, the CF_4 fraction from the
treatment gas appears first at the outlet of the second

30 column 50-2, with the NF_3 fraction appearing later. The CF_4
and NF_3 are not completely separated at this point, and a

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mixed gas containing both components is discharged in the middle. Accordingly, when the CF_4 is discharged, the valve 46 is closed, the valve 40 is opened, and $CF_4 + N_2$ is collected, when $CF_4 + NF_3$ is discharged, the valve 40 is

5   closed, the valve 42 is opened, and $CF_4 + NF_3 + N_2$ is collected, and when NF_3 is discharged, the valve 42 is closed, the valve 44 is opened, and $NF_3 + N_2$ is collected. The $CF_4 + NF_3$ fraction may be further separated using a separate column packed with activated carbon. Alternatively,

10   the $CF_4 + NF_3 + N_2$ may also be returned to the treatment gas side of the separation device.
[0031]

In this manner, $C_2F_6 + N_2$, $CF_4 + N_2$, and $NF_3 + N_2$ fractions can be collected separately.

15   [0032]

Fig. 5 shows an alternative structure for the chromatographic separation device 20. In this example, a single column 50 is packed sequentially with zeolite (molecular sieve 13X) 30 and activated carbon 32, with the

20   zeolite closer to the column inlet. Accordingly, the treatment gas first makes contact with the zeolite 30, and subsequently contacts the activated carbon 32.
[0033]

With this type of column 50, gas separation can be

25   conducted in an almost identical manner to that described above for the series-connected first and second columns 50-1 and 50-2. This example differs from that above in that C_2F_6 also passes through the activated carbon 32, but even after passage through the activated carbon 32, C_2F_6 is still

30   discharged after CF_4 and NF_3, meaning there is no deleterious impact on the separation performance. In other words, as

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shown in Fig. 6, the fractions CF_4 + N_2, CF_4 + NF_3 + N_2, NF_3 + N_2, and C_2F_6 + N_2 appear sequentially at the outlet of the column 50. Accordingly, by opening the valves 38, 40, 42 and 44 in sequence, each of the fractions can be separated

5   and recovered. The CF_4 + NF_3 + N_2 fraction may be further separated using a separate column packed with activated carbon, or may be returned to the treatment gas side of the separation device. Other facets of the structure and the operation of this example are the same as those described in

10   relation to Fig. 2.

[0034]

In this manner, by using a chromatographic separation device 20 in which the treatment gas is passed sequentially through the two fillers shown in Fig. 2 and Fig. 5, CF_4, NF_3

15   and C_2F_6 can be separated.

[0035]

In the examples shown in Fig. 2 and Fig. 5, the chromatographic separation was conducted with the zeolite 30 positioned in the former stage and the activated carbon 32

20   in the latter stage, but this sequence may also be reversed. Furthermore, in the example of Fig. 5, the zeolite and the activated carbon may also be mixed. However, tests suggest that separating off C_2F_6 first using the zeolite 30, and then using the activated carbon 32 to separate CF_4 and NF_3 leads

25   to a reliable separation, whereas if the sequence is reversed, complete separation of NF_3 and C_2F_6 may not be possible.

[0036]

As follows is a description of the separation of CF_4

30   and C_2F_6 by the zeolite 30. In this example, a zeolite 30 with a pore size of at least 0.5 nm is used as the filler.

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By using a zeolite with this type of large pore size, CF_4 and C_2F_6 can be effectively separated.
[0037]

In other words, a variety of different zeolites were
5   tested as fillers, and it was found that whereas a molecular
sieve 5A (manufactured by GL Sciences Inc.) with a pore size
of approximately 5 nm is unable to produce a satisfactory
separation, molecular sieve 13X (manufactured by GL Sciences
Inc.), and zeolite F-9 (manufactured by Tosoh Corporation),
10   which has a pore size of approximately 0.8 nm (meaning it is
unable to adsorb molecules with effective diameters greater
than 0.8 nm) and is marketed as an equivalent product to
molecular sieve 13X, are ideal for achieving separation.
[0038]

15   Currently, there are no zeolites commercially available
with a larger pore size than molecular sieve 13X, but it is
believed that a zeolite with a larger pore size than
molecular sieve 13X would also be usable, although this has
not been confirmed.
20   [0039]

For CF_4 and C_2F_6, the maximum molecular diameter,
calculated on the basis of the F-F internuclear distance and
the F electron cloud radius of 0.133 nm, is 0.4445 nm for
CF_4 and 5.69 for C_2F_6. For example, the maximum molecular
25   diameter for CF_4 is determined using the equation 0.1785
(the F-F internuclear distance) + 0.133 × 2 (two F).
[0040]

When molecular sieve 5A is used, it is thought that the
reason that separation of CF_4 and C_2F_6 cannot be achieved
30   reflects the fact that the pore size is smaller than the
molecular diameter of the C_2F_6. Accordingly, the pore size

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of the zeolite must be larger than the maximum molecular diameter of C_2F_6.

[0041]

When this type of zeolite is used, the adsorption of

5 CF_4 weakens, whereas the C_2F_6 continues to be adsorbed. It is thought that this effect is responsible for the reliable separation of the CF_4 and C_2F_6.

[0042]

A molecular sieve is normally used for separating

10 molecules that are larger than the sieve pore size from molecules that are smaller, and the conducting of a separation process using a molecular sieve with a pore size that is larger than both of the separation target materials is unusual.

15 [0043]

In this embodiment, separation of the target materials CF_4 and C_2F_6 is achieved using a zeolite with an adsorption pore size that is larger than the maximum diameter of both CF_4 and C_2F_6.

20 [0044]

In this chromatographic separation device 20, nitrogen is used as a carrier gas, and by using this carrier gas to sequentially desorb and discharge the CF_4 and C_2F_6 adsorbed to the filler, the CF_4 and C_2F_6 are separated.

25 [0045]

In another preferred configuration, a plurality of the above chromatographic separation devices 20 are prepared, and the exhaust gas is passed sequentially through each of these chromatographic separation devices 20, with each

30 fraction collected sequentially from each of the chromatographic separation devices 20.

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[0046]

The collection of each of the component gases at the outlet of the chromatographic separation device 20, and the switching of the valves, are preferably conducted in
5   accordance with the results of analyses performed on the gas at the outlet. For example, the different components can be detected using a quadrupole mass spectrometer (QMS), a differential thermal detector (TCD), or a Fourier transform infrared analyzer (FT-IR), with control then conducted in
10   accordance with the results of the analysis.

EXAMPLES

[0047]

A test was conducted using a test unit with the
15   structure shown in Fig. 7. The unit in Fig. 7 corresponds with the configuration shown in Fig. 2.

[0048]

The first column 50-1 for the test employed a column in which a 5 m long SUS pipe of outer diameter 1/8 inch was
20   packed with a zeolite 30 comprising molecular sieve 13X (manufactured by GL Sciences Inc.) with a particle size of 60 to 80 mesh. The second column 50-2 for the test employed a column in which a 5 m long SUS pipe of outer diameter 1/8 inch was packed with an activated carbon 32 comprising palm
25   shell activated carbon with a specific surface area of 1158 m^2/g and a particle size of 60 to 80 mesh. The first and second columns 50-1 and 50-2 were connected together in series.

[0049]

30   Nitrogen (N_2) gas was passed through the first and second columns 50-1 and 50-2 at a flow rate of 35 mL/minute,

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and a six-way cock 60 was used to introduce a mixed gas of
$CF_4/C_2F_6/NF_3$ ($CF_4:C_2F_6:NF_3$ = 1:1:1) in a pulse-like manner.
Furthermore, the outlets of both the first column 50-1 and
the second column 50-2 were analyzed using a mass
5   spectrometer 62.   In the drawing, MFC represents a flow rate
controller.
[0050]
The analysis results from the outlet of the first
column 50-1 are shown in Fig. 3, and the analysis results
10   from the outlet of the second column 50-2 are shown in Fig.
4.
[0051]
The test was conducted at 40°C, but other temperatures
are also acceptable.   However, because the separation
15   properties vary depending on the temperature, the test is
preferably conducted at a constant temperature.
[0052]
The test results confirmed that by using a pulsed
introduction of gas, the respective peaks for the CF_4 + NF_3
20   mixture and C_2F_6 had completely separated by reaching the
outlet of the first column 50-1, meaning that by simply
selecting the sampling period, a CF_4 + NF_3 mixed gas and pure
C_2F_6 could be obtained.   Accordingly, the C_2F_6 was extracted,
and the CF_4 + NF_3 mixed gas was fed into the test column 2.
25   As a result, it was found that at the outlet of the second
column 50-2, the CF_4 and NF_3 had separated by the time of
discharge.
[0053]
At the outlet of the second column 50-2, pure CF_4, an
30   unseparated CF_4 + NF_3 gas fraction, and pure NF_3 were
obtained, and the unseparated gas fraction is preferably

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either returned to the inlet of the series-connected first and second columns, or passed through a separate activated carbon column provided in series, to effect separation and recovery.

5 [0054]

Hence, the unit described above was confirmed as being capable of favorable recovery of CF_4, C_2F_6, and NF_3.

[0055]

(Example 2)

10 A test was conducted using a test unit with the structure shown in Fig. 8. The column 50 for the test employed a column in which a 10 m long SUS pipe of outer diameter 1/8 inch was packed first with palm shell activated carbon with a specific surface area of 1158 m^2/g and a

15 particle size of 60 to 80 mesh, and then with molecular sieve 13X (manufactured by GL Sciences Inc.) with a particle size of 60 to 80 mesh. This yielded a column such as that shown in Fig. 5, in which the zeolite (molecular sieve 13X) 30 and the activated carbon (palm shell activated carbon) 32

20 were arranged in sequence along the flow direction of the treatment gas. The packing ratio of the two fillers was 1:1.

[0056]

Nitrogen gas was passed through the column 50 at a flow rate of 35 mL/minute, and a six-way cock 60 was used to

25 introduce a mixed gas of $CF_4/C_2F_6/NF_3$ (CF_4:C_2F_6:NF_3 = 1:1:1) in a pulse-like manner. The outlet of the column 50 was analyzed using a mass spectrometer 62. In the drawing, MFC represents a flow rate controller.

[0057]

30 The analysis results from the outlet are shown in Fig. 6. The test was conducted at 40°C, but other temperatures

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are also acceptable. However, because the separation
properties vary depending on the temperature, the test is
preferably conducted at a constant temperature.
[0058]

5   The test results revealed that the peaks for CF_4, NF_3,
and C_2F_6 appeared sequentially at the outlet of the column 50,
confirming that each of the gases could be separated. The
unseparated $CF_4 + NF_3$ fraction can be separated by passage
through a subsequent, separate activated carbon column.
10   [0059]

The width of the peaks and the level of overlap of the
unseparated portion vary depending on the concentration of
the supplied gas, but a satisfactory separation can be
achieved by altering the packing ratio (in this example 1:1)
15   of the fillers packed inside the single column.
[0060]

In this manner, the unit described above was confirmed
as being capable of favorable recovery of CF_4, C_2F_6, and NF_3.
[0061]

20   Tests were also conducted using F-9 (manufactured by
Tosoh Corporation), which is described as having a similar
structure to molecular sieve 13X (an equivalent product), as
the zeolite 30. This F-9 enabled separation of CF_4 and C_2F_6
in a similar manner to that observed for the molecular sieve
25   13X, although the retention times were marginally longer.

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